

Influence of density and temperature on the microscopic structure and the segmental relaxation of polybutadiene

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We investigate the influence of temperature and density on the local structure and the dynamics of polybutadiene by controlling both, hydrostatic pressure and temperature in neutron diffraction experiments on deuterated polybutadiene up to 4GPa, in inelastic incoherent scattering experiments on protonated polybutadiene for the fast dynamics and in high precision calorimetry for the slow process. We observe that the static structure factor $S(Q)$ does not change along macroscopic isochors. This behavior is contrary to the relaxations observed on the ns- and ps- time scale and viewed by the dynamic incoherent scattering law $S(Q,\omega)$, which differ strongly along the same thermodynamic path. We conclude that the static behavior, i.e. $S(Q)$, is dominated by macroscopic density changes, similar to the vibrational excitations in the meV-range. However, the relaxation dynamics is more sensitive to thermal energy changes. This is confirmed by the finding that lines of identical (in time, shape and Q-dependence) relaxation behavior, isochrones on the 10^{-9} sec time scale, clearly cross the constant density lines in the P,T-plane. Concerning $S(Q)$, we can reasonably relate the variation of the main-peak position to the average neighbor chain distance and deduce crude microscopic thermal expansion and compressibility coefficients, with a direct link and good agreement to the thermodynamic analysis.